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The effect of pressure on the autoignition of
octahydro -1,3,5,7,- Tetranitro,
-1,3,5,7,-Tetrazine (HMX)

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Monterey, California. U.S. Naval Postgraduate School

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THE EFFECT OF PRESSURE ON THE
AUTOIGNITION OF OCTAHYDRO-1,3,5,7,
-TETRA-NITRO, -1,3,5,7, -TETRAZINE (HMO)

WILLIAM MARLOWE TRUESDELL

THE EFFECT OF PRESSURE ON THE
AUTOIGNITION OF OCTAHYDRO-1, 3, 5, 7,
TETRANITRO,-1, 3, 5, 7,-TETRAZINE (HMX)



by

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ABSTRACT

The autoignition of HMX under various conditions of initial pressure yields a family of curves similar to those encountered in rate of burning studies of propellents. From this a hypothesis that the two phenomena are coupled is developed. A description of current theories of thermal decomposition of explosives, autoignition techniques, and the polymorphs of HMX is presented. A new machine for sealing standard Pyrex melting point tubes under various conditions of initial pressure is described.

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TABLE OF SYMBOLS

ρ	- density of explosive, g/cm
Q	- heat of reaction, cal/gm
Z	- frequency factor, sec^{-1}
E	- activation energy, cal/gm-mole
R	- universal gas constant, cal/g-mole $^{\circ}\text{K}$
T	- absolute temperature, $^{\circ}\text{K}$
λ	- thermal conductivity, cal/cm sec $^{\circ}\text{K}$
∇	- Laplacian operator
C	- specific heat of explosive, cal/g $^{\circ}\text{K}$
t	- time, sec
a	- half thickness of explosive or radius of cylinder or sphere, cm
δ	- dimensionless reaction rate
γ	- ratio of the specific heats
T_0	- temperature of the hot spot, $^{\circ}\text{K}$
A	- maximum available energy
B	- product
C	- heat capacity, cal/gm-mole
h	- Planck's constant
ΔS^*	- entropy of activation, e.u.
K	- Boltzmann's constant
ΔH^*	- heat (energy) of activation, cal/gm-mole
f	- fugacity

1. Introduction

The basic mechanism which leads to the ignition of explosives is not clearly known. It is the purpose of this thesis to present the currently accepted theories and then, through autoignition techniques using octa-hydro - 1,3,5,7; tetranitro - 1,3,5,7; tetrazine (HMX), to show a correlation which may exist between burning and ignition.

The first section of the work deals with the mechanism of thermal decomposition leading to explosion and with autoignition techniques. The remainder of the work deals with HMX and the techniques used to arrive at this correlation between rate of burning and ignition.

2. The Mechanism of Thermal Decomposition Leading to Explosion

There are many ideas concerning the sequence of events which lead to explosion or detonation. As of this writing the general thread which connects them all is the thermal theory of explosions. This idea was developed by Frank - Kamenetsky¹ and is sometimes called the critical-conditions-for-explosions concept. Its basis is that an explosion results when the rate of heat production is greater than the rate of heat dissipation to the surroundings. It can be expressed as a differential equation:

$$\rho Q Z e^{-E/RT} = -\lambda \nabla^2 T + \rho C_1 \frac{dT}{dt} \quad (1)$$

heat generation by chemical reaction	heat loss by conduction	self-heating
---	----------------------------	--------------

which has been solved for the steady state condition for a slab with both faces held at constant temperature¹; for the cylinder and the sphere with their outer surfaces held at constant temperature³; and the hollow cylinder with its surfaces at constant temperature⁴ and with its exterior surfaces at a constant temperature and its interior surfaces

adiabatic⁵. Recently the solution for the transient condition has been obtained^{6,7} and, knowing four parameters:

1. a , the half thickness of explosive or radius of cylinder or sphere
2. $\rho QZE/\Lambda R$ in $^{\circ}\text{K}/\text{cm}^2$
3. E , the activation energy
4. δ , the critical value of the shape factor, (or reaction rate, dimensionless)

the critical temperature and time to explosion may be obtained from a nomograph^{8,9} if the physical properties of the explosive are as described by the mathematics. Generally they are not but the results still give a fair approximation of the critical temperature (usually lower than the experimental temperature) and time to explosion. The reason for this impreciseness rests in, first; accurately determining the parameters involved, such as E and those which vary with temperature, second; if the explosive is a uniform solid, third; understanding what true mechanism is involved in the events leading to explosion. To determine these mechanisms we will examine two of the theories of the mechanism leading to explosion and also some of the autoignition apparatus used to determine the time-temperature relationship leading to explosion.

The first theory we will deal with is the Hot Spot Theory advanced by Bowden and Yoffe^{10,11} which says that the initiation of the explosion train is at a "hot spot" which can be grit, gas bubbles, or any local disturbance which would allow crystal strain energy to accumulate. This energy accumulation would be enough to cause molecules of the explosive to decompose, releasing energy and spreading in a chain reaction.

Bowden's first experiments dealt mainly with impact, with the explosive sensitized by gas bubbles and grit particles. He postulated and showed experimentally that if the grit particles have a melting point higher than that of the explosive the sensitivity of the explosive to shock is increased, or that sensitivity increases with the increase of the grit's melting point. He also showed that, as expected, hardness, size and the thermal conductivity of the grit particle had an effect on the sensitization of the explosive. The reason the particles concentrate energy is that, on impact, one of the only ways for the explosive to dissipate the energy it has received is through melting, hence the highest temperature it will reach is that in the melted state if any solid remains. However, if the grit's melting point is higher, then the energy accumulation at the grit may be higher and can cause initiation. Representative figures, experimentally found by Bowden, for secondary explosives (i.e. HMX, MP ~ 276 C (13)) would be a grit melting point of 400 - 500° C and for primary explosives (i.e. lead azide (PbN_6), lead styphnate ($\text{PbC}_6\text{H}_3\text{N}_3\text{O}_9$) which decompose and explode before melting 260 - 310°C) a melting point of greater than 500° C.

The effect of gas bubbles on impact sensitivity was postulated to be caused by the rapid or sudden increase in pressure, causing a corresponding increase in the temperature of the entrapped gas which results in a possible explosion. Many experiments were conducted and it was shown that the pressure of gas bubbles did sensitize the explosive. Also when the pressure around the explosive was increased to 20 atm., or decreased to vacuum, a decrease in the sensitivity resulted. This was explained by the formula for an ideal gas:

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (2)$$

where γ is the specific heat ratio. If p_1 is increased, a correspondingly higher p_2 can only be reached by increasing the energy imparted to the system. If the pressure is decreased, T_2 will increase but as there will be less trapped gas in the bubbles the corresponding amount of energy developed is lower. Experimental evidence corresponded to the change in sensitization predicted.

Bowden also noted the work of Garner (1938) who said that at least two adjacent molecules are required to decompose simultaneously for the initiation of explosion.

A recent test of this theory¹³ was made using irradiation of explosives as suggested by Bowden. RDX, HMX, PETN and Nitroglycerine (NG) were irradiated at elevated temperatures (125°C - 215°C). It was hypothesized that pion capture would result in local temperatures up to 1500°C in a 100°A radius cylindrical volume and that this would be sufficient to initiate explosion. In addition, work done by Dodd¹⁴ showed that on a statistical approach the simultaneous decomposition of only ten adjacent molecules in about 10^{-6} seconds is sufficient for initiation, hence it was calculated that in all cases initiation should occur. It did not. It must be noted, however, that Bowden² said that a critical size of 10^{-5} cm. must be exceeded for their model to be applicable, however, it is not apparent how the limitation was arrived at from the mathematical model itself.

A second theory on the mechanism of the thermal ignition of explosives was advanced by A. F. Belyaev in 1946,¹⁵ about six years prior to Bowden's publication. He stated that the volatility of the explosive has the greatest effect on the facility of ignition as the main reaction which controls the rate of combustion occurs in the gas phase. He showed

experimentally that the temperature of the explosive (TNT) at ignition is generally at or above a theoretical boiling point, hence he concluded that ignition occurred in the gas phase. The temperature of the vapor phase was the critical parameter, and not the temperature in the liquid phase (which would not exceed the boiling point at the local pressure). To explain ignitions which occurred in the liquid phase, he noted that bubbles from boiling were probably present, hence ignition occurred in them. In almost all of the cases when ignition occurred in his apparatus, it occurred well above the melt and in the vapor phase.

The theory actually fits in with the "hot spot" theory, and Bowden states in his work¹⁰ that there is a possibility that ignition does occur within the gas bubbles. To correlate this with the grit, one only has to note that the melting points of the grit to assure ignition were all from 400° -600° C which would be in, or greater than, the range of the theoretical boiling points of the explosives tested.

Recent work in explosives has related the rate of heat dissipated by melting directly to the sensitivity of explosives.¹⁶ Using four secondary explosives; TNT, tetryl, RDX and PETN, formed into strands and pressed against a hot plate, Chaiken and his coworkers were able to measure the rate of regression through viscous flow of the explosive and from this obtain the rate of the dissipation of energy of the explosive. They found the rate of dissipation of energy through melting to be TNT > tetryl > RDX > PETN, which is the order of increasing sensitivity of the explosives. This information, when coupled with the "hot spot" theory, suggests that the melting point of the explosive when compared to the grit is not the important factor, but the rate at which heat can be dissipated through melting is important. No work has been done, however, to correlate energy dissipated through vaporization

of the explosive and correlate this with sensitivity.

It was noted earlier that increasing the ambient pressure of a liquid explosive decreased the sensitivity because of a corresponding decrease in ΔT of the entrapped gas bubbles. The substance used was nitroglycerine. A series of studies in the USSR has shown that the mechanism for thermal decomposition leading to explosion is pressure sensitive and depends greatly on decomposition products and other agents.¹⁷ (See Appendix I) Hence the desensitization at reduced pressure may be explained by a reduction of these fairly volatile substances in the N.G.. It has been shown¹⁷ that for PETN, prolonged heating at reduced pressure actually decreases its sensitivity as the impurities or decomposition products are removed (as shown by an increase in melting point). Because of such autocatalytic effects, especially in C-H-N-O explosives, another technique for examining explosive time-temperature behavior is needed. We will examine some of these autoignition techniques.

3. Autoignition Techniques

The first autoignition techniques of record were in the early 1900's and the explosive used was cellulose nitrate. In most of these cases the explosive was heated slowly to the temperature of explosion. Because of the differences in production methods and the questionable purity of the "gun cotton" the tests were not too successful.¹⁸ Later work with nitrate esters varied the heating rates and atmospheres and it was found that the ambient gas was not important but the heating rates were very important.

One common autoignition technique is placing the explosive in question on some sort of heat source, which might be a large metal block²⁰ which can be heated at a constant rate. This technique is varied only by the efficiency of the energy transfer and measurement.

Another common technique is plunging the explosive into a hot bath of molten metal, oil or salt. This technique was used by Ubbelohde²¹ who showed that $\log \tau$ (the time delay to explosion) vs. $1/T$ was a straight line and from this the following equation was established:

$$\log_{10} \tau = A/T_o + B$$

where T_o is the temperature of the hot spot (3)

$$A = \Delta H^*/R \quad \text{and}$$

$$B = \log_{10} (C h e^{-\Delta S^*/R} R T_o / Q R f \Delta H^*)$$

C = heat capacity

h = Planck's constant

ΔS^* = entropy of activation

Q = heat of explosion

R = Boltzmann's constant

ΔH^* = heat of activation

f = fugacity

It can be easily seen from the above equation that the slope of the line is $\Delta H^*/R$, hence the apparent activation energy may be taken directly from the plotted time-temperature relationship. From this and impact data Cook²¹ estimated that all CHNO explosives have a ΔH^* of between 30 and 36 Kcal/mole, which is reasonable if one agrees that all explosives exhibit similar kinetics under similar circumstances, as there are no other properties they would hold as a class. However, Macek²² shows that even for such a common explosive as Teteryl, activation energies of 52.0, 38.4, 34.9, and 14 Kcal/mole are reported in the literature with a corresponding disparity in frequency factor (Z , sec.⁻¹). The main reason for this range is that no rate expressions for even the simplest explosives have yet been broken down into Z and the exponential term. Usually they are only estimated with the above equation.

One reason why analytical methods do not generally fit reality is that they do not take into account melting, autocatalysis, impurities present, or any other kinetic data, and for this reason they give only that energy required for that specific initiation under those given conditions.

An error that appears with frequency in the literature is that the temperature of the explosive is not measured directly but is correlated with the temperature of the bath. Belyaev (Belyayev)¹⁵ showed that an explosive seldom reaches temperatures in excess of its boiling point; hence all high temperature work (>500°C) where the explosive temperature is not measured directly generally gives data which is difficult to work with as one does not know the physical state of the explosive. It is for this reason that most work done in this paper is in the lower temperature region.

A survey of the other autoignition devices used in the United States may be found in reference (24). They are not included in this paper as most are classified.

4. HMX and its Polymorphs

Octahydro - 1,3,5,7: tetranitro - 1,3,5,7; tetrazine ($C_4H_8N_8O_8$), or HMX, is a secondary explosive which has a large variety of uses in the military, most of which are classified. It is generally found in combination with other components which act as binders. It cannot be melt cast as it generally decomposes explosively at its melting point, about 276°C. It first came to light as an impurity in RDX processed during World War II. It was discarded until it was noted that because of its higher density (1.9 g/cc. vs. 1.8 g/cc. for RDX) it would have better characteristics as an explosive than RDX.

HMX is prepared in the laboratory from the nitration and cleavage of

hexamine. The commercial grades of HMX differ in purity, especially between British and American; the British grade generally contains little RDX while the American grade may have up to 5%. All HMX used in this work was American produced HMX recrystallized from acetone.²³

There are four polymorphic forms of HMX: alpha, beta, gamma, and delta, the most stable form being beta. The temperature stability ranges for these polymorphs are found in Table I.²⁶ The structure of beta-HMX is shown in figure 1.²⁷ The crystal shapes of the polymorphs are as follows:

beta - generally "massive" and well-formed - sometimes a rod-like habit with well-formed ends is observed.
(Fig. 2).

alpha - compact mass is of fine needles of approximately the same orientation - have a striated appearance which characterizes them from the rod form of beta.
(Fig. 3).

gamma - flat triangular plates. (Fig. 4).

delta - cigar shaped with extra piece at end (from solution) or barrel shaped (from sublimation).
(Fig. 5 with gamma).

If commercial grades of HMX are viewed under a microscope, alpha, beta, and gamma HMX are usually always present (along with RDX). RDX, when recrystallized from acetone, is easily differentiated from HMX.
(Fig. 6).

The purity of HMX can be estimated or determined in a variety of ways.^{28,29} One of the simplest methods is thin layer chromatography³⁰ which was used in this work.

TABLE I

Temperature Stability Ranges of the Polymorphs

<u>β-HMX ($^{\circ}\text{C}$)</u>	<u>α-HMX ($^{\circ}\text{C}$)</u>	<u>γ-HMX ($^{\circ}\text{C}$)</u>	<u>δ-HMX ($^{\circ}\text{C}$)</u>
R.T. to 146-150	146 150 up to 156-158.5	metastable	156 158.5 to mp
" " 115	115 " " 156	156 $^{\circ}$	156 " "
" " 105	105 " " 155	metastable	155 " "
" " 102-104.5	102 104.5 " 160-164	"	160-164 " "

(Literature values from Reference 26.)

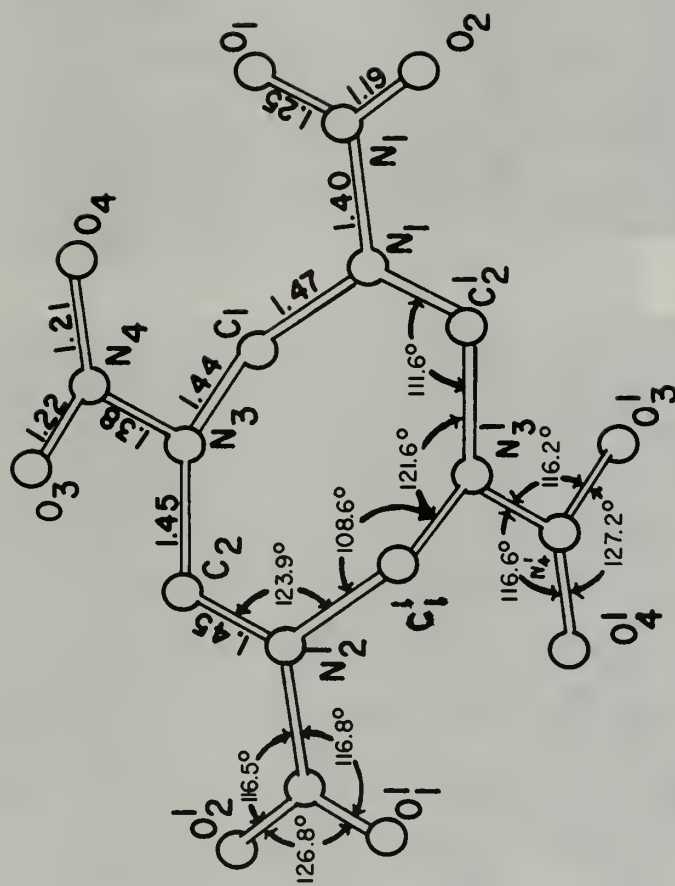


FIGURE 1. BOND DISTANCE AND ANGLES
IN HMX



DELTA-ONE (10X)
FIGURE 2



ALPHA-ONE (100X)
FIGURE 3



Gamma-ray (100X)

FIGURE 4



Delta-ray (with beam, 400X)

FIGURE 5



RDX (40X)
FIGURE 6



Sealed tube (20X)
FIGURE 7

5. Description of Apparatus

Apparatus previously described³¹ uses 1mm standard Pyrex melting point tubes (which contain a small amount of explosive) to determine the thermal sensitivity and autoignition characteristics of explosives. It does this by plunging the tube into a bath of molten salt and measuring the time to explosion. To determine autoignition characteristics under various conditions of initial pressure, a tube sealing device was constructed. This device can seal 50 tubes at pressures from about 1 torr to in excess of 1200 psi in four minutes.

The general description of the apparatus is shown in figure 7.

The description of the tube sealer is shown in figure 8. The tube sealer is placed in a pipe which can then be evacuated or pressurized, as desired.

Approximately 130v are delivered to the transformer which converts this to 500 amps and about 10 volts. This current is fed through water-cooled, one-quarter inch, copper tubing (a) to the tube sealing device. The tubing is interrupted at (d) where rubber tubing carries the water between the two terminals. The current then passes through a two-percent thorium-tungsten rod (c) (used in heliarc welding) heating it to almost incandescence. The bottom platform (i) which is detached from the rods in this view has a one-quarter rpm motor (h) mounted on its bottom. This motor is energized by passing 115 volts through two terminals (b) which feed current to the motor through the two leads (g) which are not shown connected in this figure. This drives a cylindrical piece of firebrick, mounted between two round aluminum plates (e), which is drilled with fifty holes which hold the melting point tubes (f). This carries them in a circle, and they touch the thorium-tungsten rod midway between

the two terminals (j). About one-tenth of an inch or less of the top of each tube makes contact with the rod. Pressure or vacuum is introduced through (L).

The whole operation, after the variac is energized, takes about four minutes, or one revolution of the tube holder (e).

The capillary tubes sealed in this apparatus have withstood pressures in excess of 1200 psi. The seal is clean but slightly tapered (see Fig 9).

In twenty tests to see where the tube, which was under 350 psi, would fail when exposed to extreme heat, only once did the failure occur at the seal.

6. Experimental

1) Purification of HMX: Commercial grade HMX was dried, dissolved in acetone and precipitated from solution by addition of H_2O . After filtration the process was repeated. The recovered HMX was dried in a vacuum oven at $70^\circ - 90^\circ C$ for twelve hours. This was then checked for purity by thin-layer chromatography. 30 gms Silica Gel G and 60 ml of distilled water was shaken together to make a slurry and applied to glass plates. The layer was 250 thick. The plates were developed by the ascending technique using 250 ml of a 40:60 acetone - petroleum ether (b.p. $60^\circ - 80^\circ C$) solvent. Development time was about 10-15 minutes and the HMX had moved about half-way up the plates (samples were $\sim 10 \mu l$). The plates were then sprayed with a one percent solution of diphenylamine in methyl alcohol and exposed to UV light for about thirty minutes. The nitramines appeared blue-violet against a brown background. This method will detect $.02 \mu l$ of RDX in HMX. None was detected. A test blank was run with RDX present and RDX was detected.

2) Preparation of beta-HMX: The HMX prepared above was checked microscopically and found to be beta-HMX, as was expected. A hot solution of HMX in acetone when precipitated by addition of H_2O will first form gamma-HMX unless it is stirred for a short length of time. Once beta-HMX forms all the gamma-HMX is converted to beta.

3) Preparation of alpha-HMX: Four grams of beta-HMX as formed above are weighed out and approximately one-half is added to 80 ml of concentrated (70%) HNO_3 in a 125 cc Erlenmeyer flask. The mixture is slowly heated on a grounded hotplate and allowed to go into solution. As this occurs more HMX is added, a little at a time, until all of the HMX has been added. There is some fuming (white) and the heating is done in a hood with as little light present as possible (to avoid the decomposition of the HNO_3). As soon as solution is complete the flask is removed from the hot plate and wrapped in rags and a thermometer inserted. When the temperature has fallen to $30^\circ C$ (in about one and one-half hours) the solution is vacuum filtered and washed with distilled H_2O until free from acid. The product is vacuum dried in an oven at $70^\circ C$ for about six hours. It is then stored in a desiccator until ready for use.

4) Preparation of gamma-HMX: Dissolve .5 gms of HMX in 140 cc of 50% acetic acid in a 250 ml Erlenmeyer flask by gentle heating. After all the HMX is in solution cool by swirling in an ice water bath. After about three minutes, filter and wash with distilled water. Dry as with alpha-HMX.

5) Preparation of delta-HMX: Dissolve .2 gms of HMX in 30 cc of glacial acetic acid in a 100 ml Erlenmeyer flask. Cool as with gamma but filter after about 30 seconds. Wash and dry as with gamma. Delta-HMX formed in this manner will revert to beta-HMX immediately if disturbed or if any beta-HMX is present.

6) Preparation of glass tubes: One mm standard Pyrex melting point tubes are cut to about ten cm lengths and flame sealed at one end. The tubes are then vacuum dried in an oven at 70°C for over 12 hours. After the tube cools the HMX may be scooped into the tubes from a watch glass. About five tubes may be filled at one time. The tubes are small enough so the weight of explosive may be estimated from the amount in the tube to .1 mg when compared with a standard. Most samples thus prepared are about .2 mg or larger. The tubes are then sealed in the tube sealing device.

7) Sealing the tube: Half of the tubes are placed in the merry-go-round holder and placed on the turntable. The rest of the tubes are then added and the entire section (Fig. 8) is placed in a tank and bolted in place. The pressure tubing and electrical tubing and leads are connected and the tank is evacuated and water turned on. If pressure is desired, then Helium is slowly introduced to the tank, purged, and reintroduced and brought up to the desired pressure. The heating element is energized, and after about ten seconds, the turntable is energized. After slightly more than four minutes the turntable is shut off and the heating element also. After the tank has returned to one atm all connections are disengaged. The sealer is removed from the tank and the tubes are carefully removed from the merry-go-round and stored for use.

8) Measuring time to explosion: The tubes are plunged into a molten salt bath which can be varied in temperature to in excess of 1000°C. A relay starts a timer immediately upon immersion and a photocell picks up any flash, or a microphone any sound, of explosion and stops the timer. This apparatus has been previously calibrated and it was determined

experimentally that the glass tubes equilibrate with the salt bath within about fifty milliseconds, well below the normal range of error encountered in the experimental data. A more detailed treatment of this apparatus is in reference (31).

7. Discussion of Results

Figure 10(a) shows the time-temperature curves at various conditions of initial pressures for beta-HMX. A total of six data points was taken for each curve. These were at 295, 324, 350, 380, 400, and 480°C. At each temperature and pressure twelve to twenty runs were taken and the time averaged. Because of the nature of the experimental errors involved, the deviation from these average times ranged from about ten to twenty percent, usually in the direction of increased time to explosion. There was no statistical way to eliminate any trials which might have been explained by cook-off, hence all runs were included. Even so, separate runs made on different days where the tubes were pressurized separately and the bath temperatures differed by about 2°C gave averages that were within 4.4% of each other.

Figure 10(b) shows the time vs $1/T$ curves usually encountered in autoignition work. There are actually two straight line portions encountered in the curves for HMX, the lower part extends from 0 to about $1.3 \times 10^4 / ^\circ K$ and the upper from $1.3 \times 10^4 / ^\circ K$ up to near the melting point of HMX. The upper portion of the curves as drawn gives an apparent activation energy of about 15 Kcal/mole. In and of itself this value is fairly meaningless.

To determine if alpha-HMX differed in its characteristics from beta-HMX, a series of runs was made at 350°C at the different pressures. The averages for 0, 100, 200, and 300 psig fell exactly on the points for beta-HMX. Not enough runs (six) were made at 400psig to give a usable

result, but it was within experimental error (1.70 vs. 1.65 sec.).

It is obvious from figures 10(a) and 10(b) that an increase in the ambient pressure decreases the time to explosion for a given temperature. To determine if this was only true for HMX, Halex No. 14 (a pyrotechnic which is a mixture of zirconium, chlorates, and other materials generally found in pyrotechnics, but no nitro compounds) was subjected to the same techniques at 350°C. Figure 12 shows the atmospheric pressure curve which was done by Professor J.E. Sinclair of this school, and the triangles denote this work. The general trend of decreased ignition times with increased pressures is again apparent.

Figure 1 shows a time vs. pressure plot. When these curves were matched, one with another, it was apparent that they had approximately the same slope. Thus they follow some general relation

$$\log T = B_1^1 p + A_1^1 \quad (4)$$

where B_1^1 is the slope of the line and A_1^1 is the intercept. Of great interest, at this point, is that the same form of equation appears in propellant literature³² showing how burning rate, r , is dependent upon pressure. In this case burning rate increases with increasing pressure.

$$r = B_2 p + A_2 \quad (5)$$

This equation is only an approximation and $\log r$ gives a better correlation. As the slopes are close to zero, the difference between r and $\log r$ is slight. It is also of interest that most propellents yield a family of curves for burning rate vs. pressure similar to figure 12. The Russians¹⁷ have also shown this linearity between burning rate and pressure and showed that there is a strong possibility that burning occurs in the vapor phase for RDX and that, if so, the reaction is bimolecular.

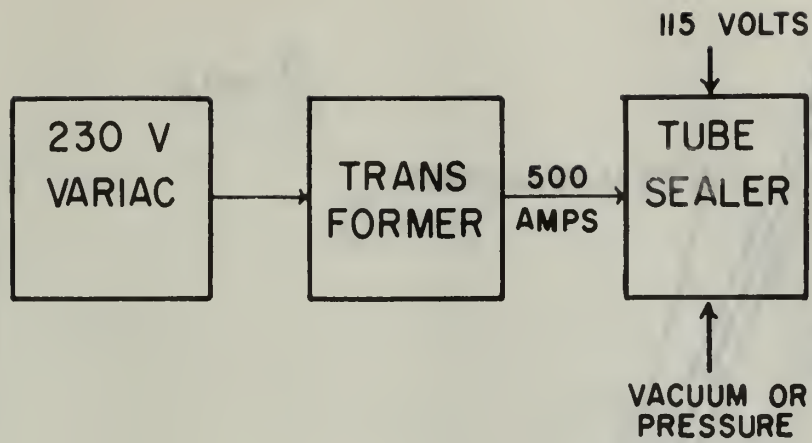
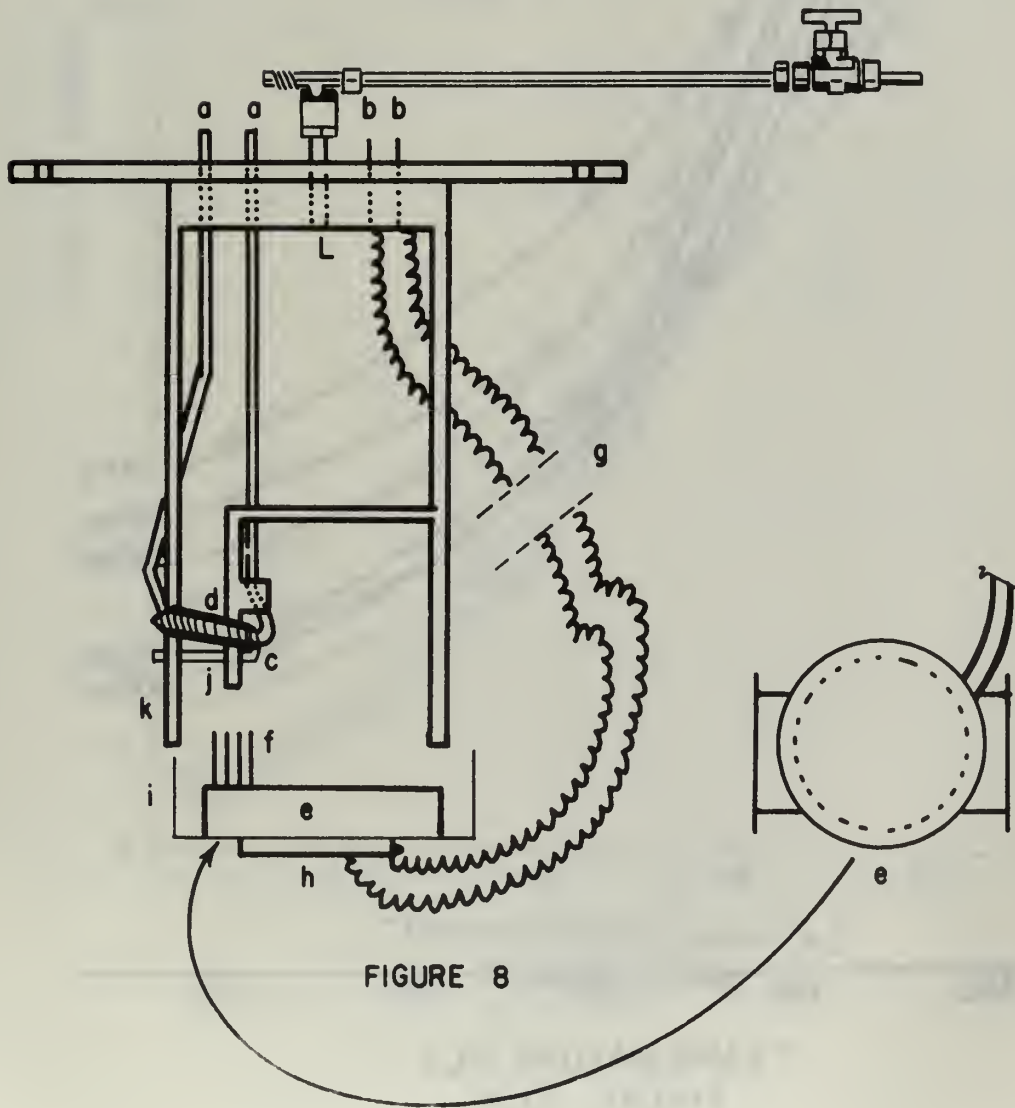


FIGURE 7



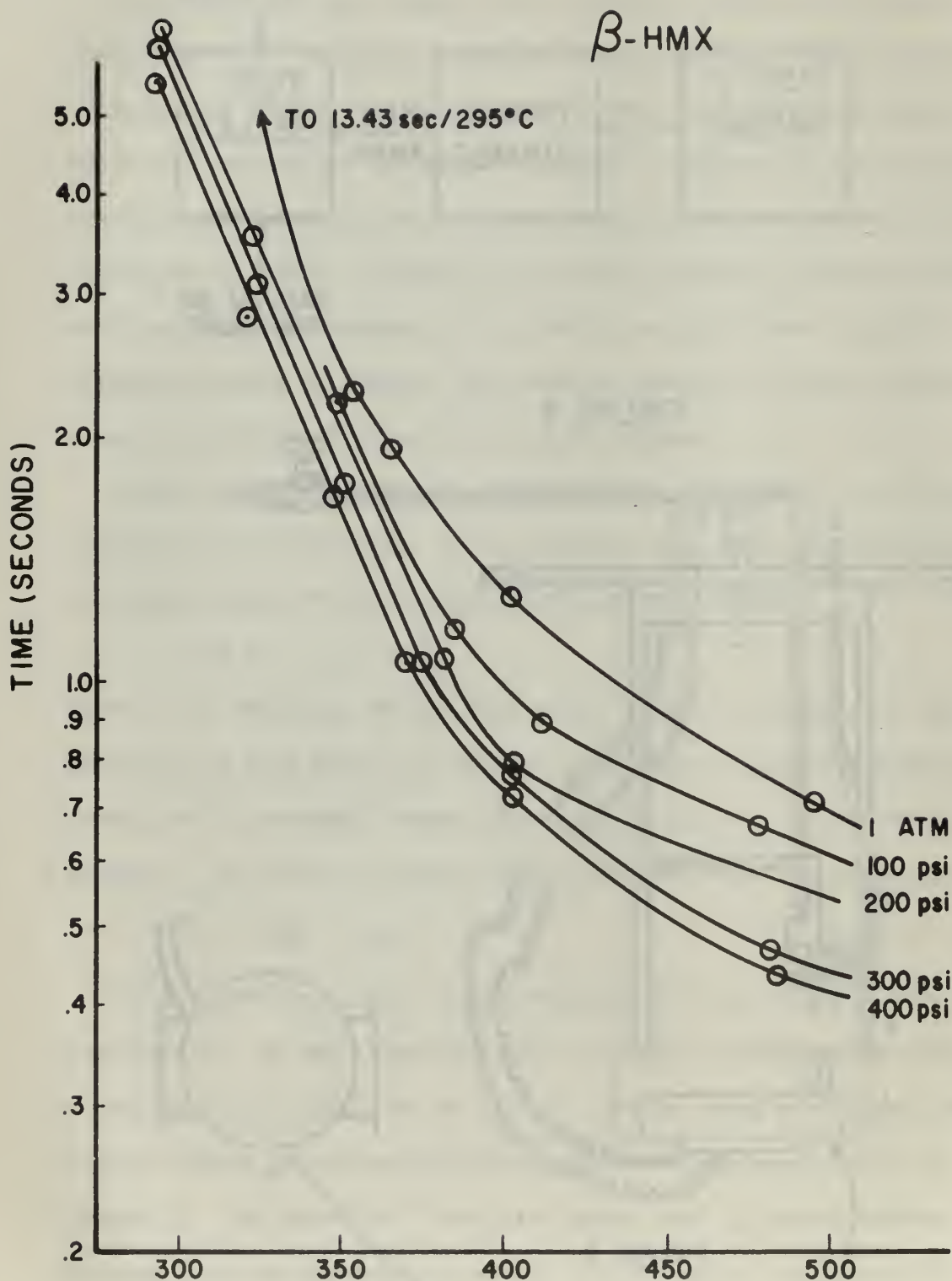
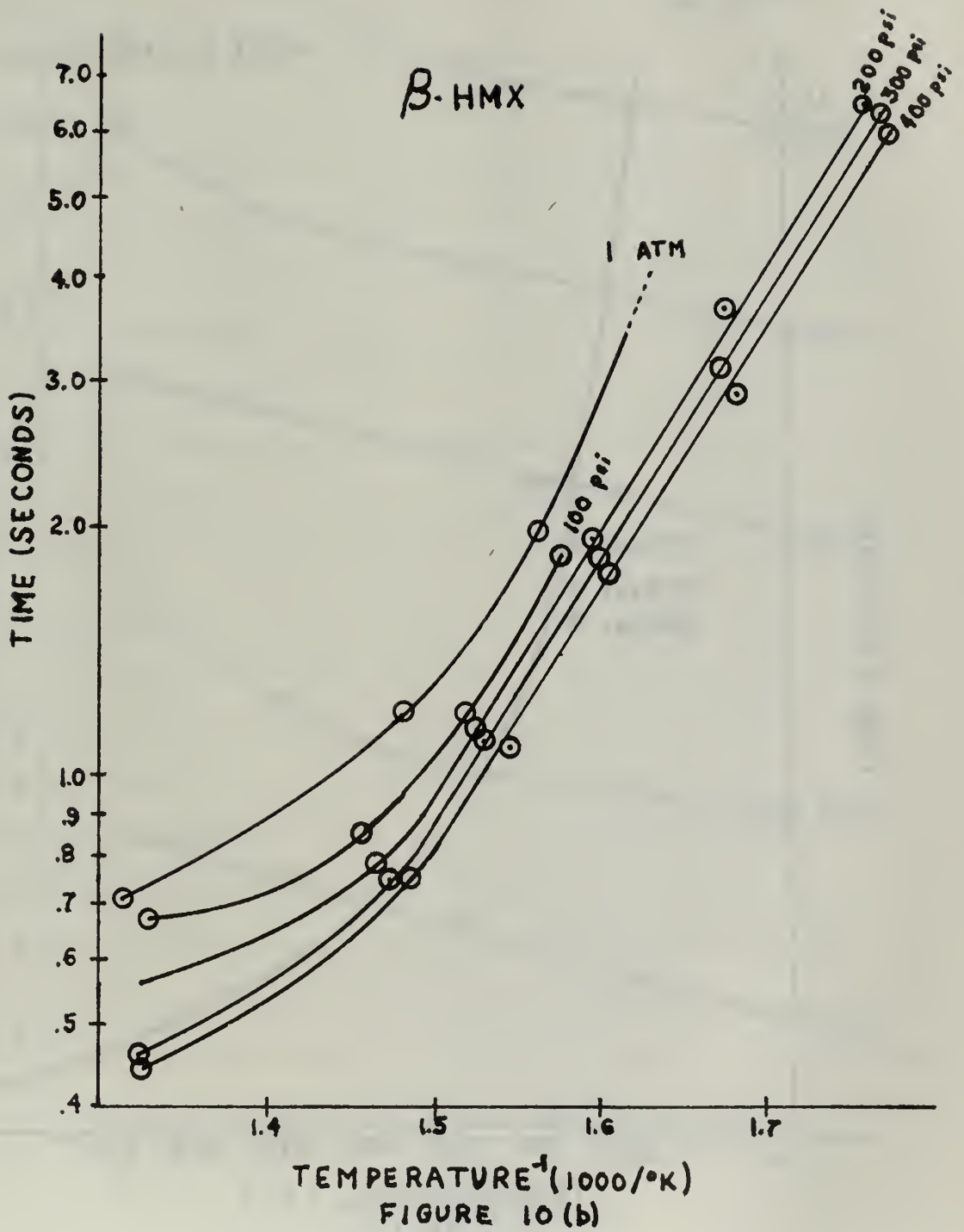


FIGURE 10 (a)



HOLEX (ref. 31)

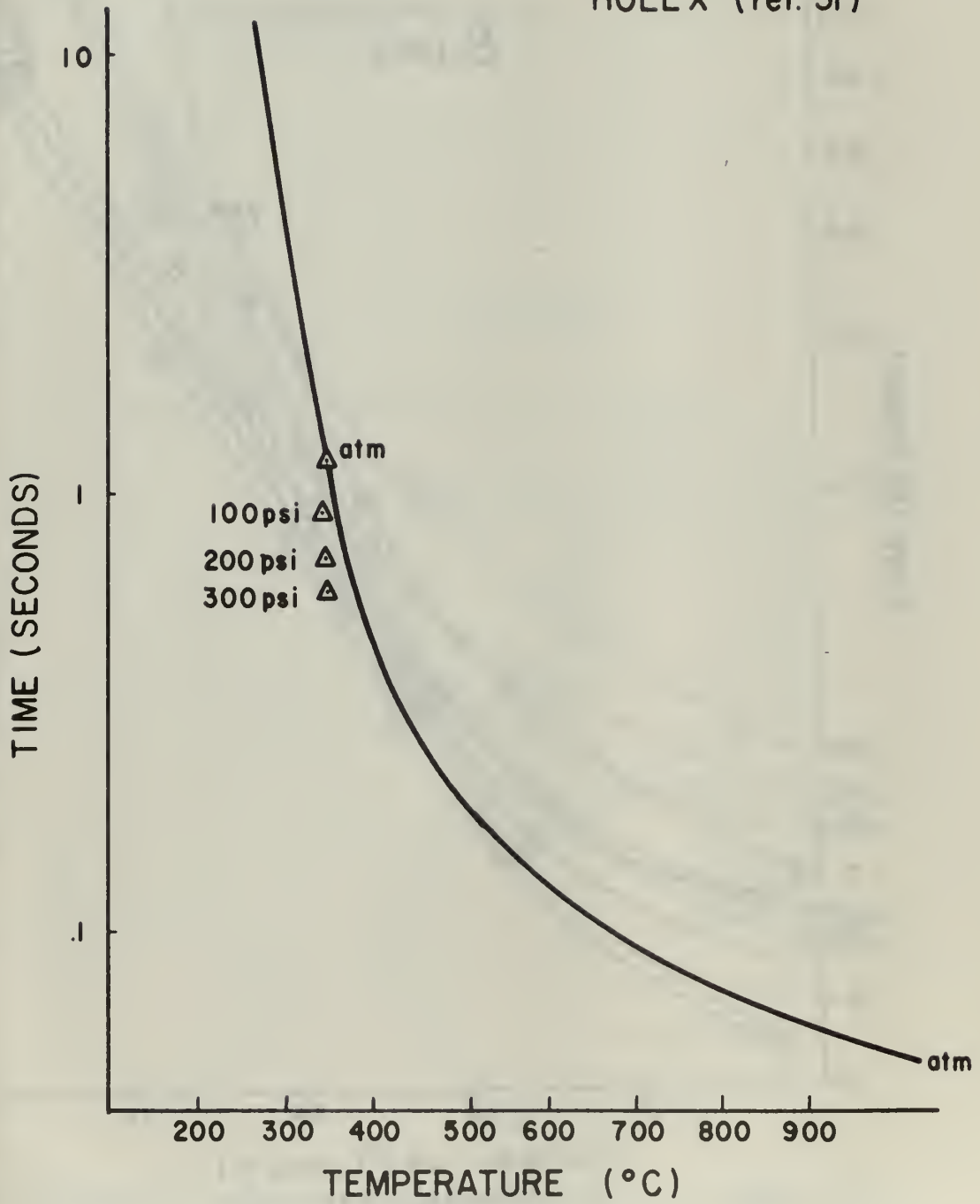


FIGURE 11

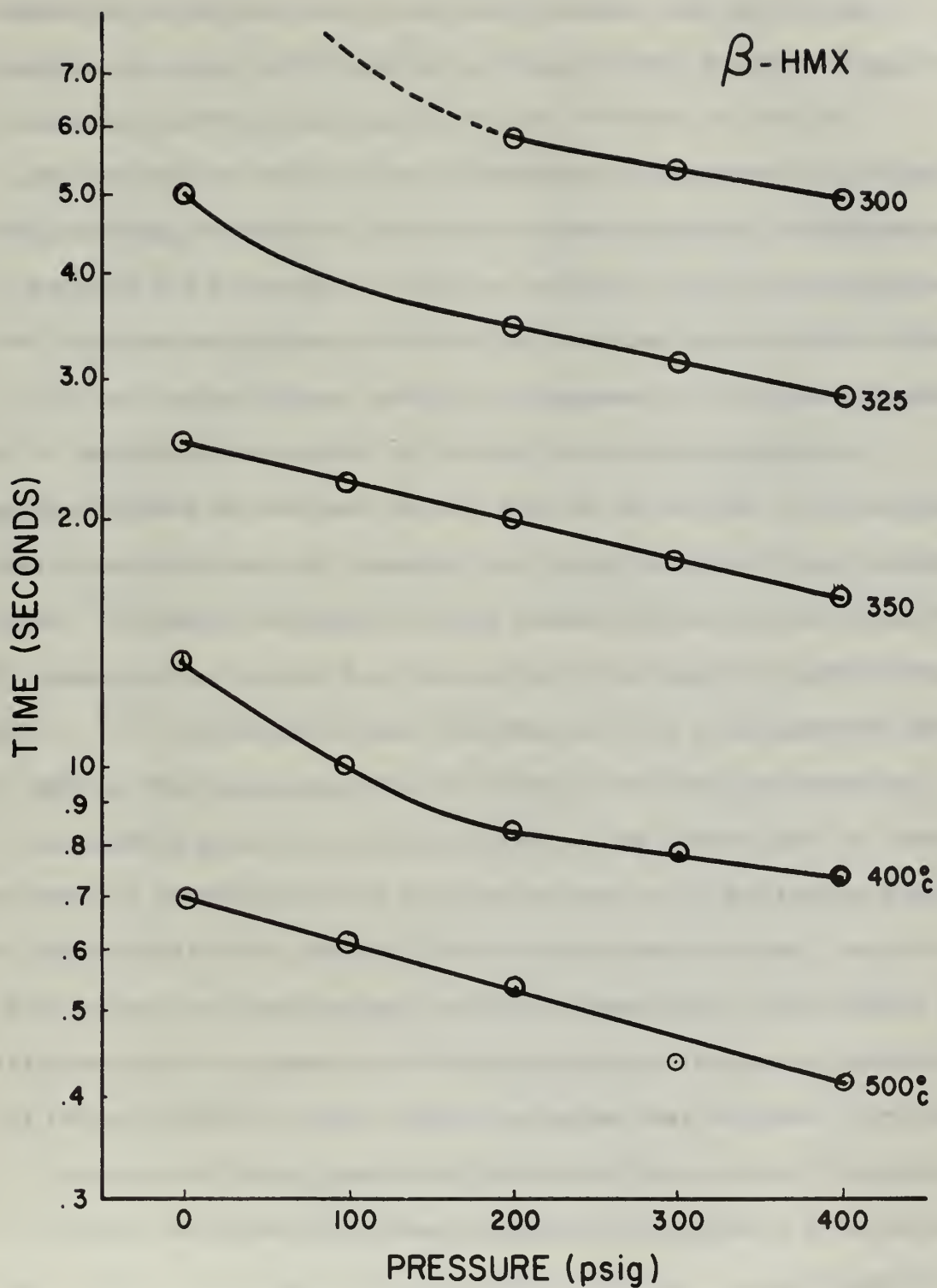


FIGURE 12

8. Conclusions and Acknowledgements

In general we have shown only trends as the temperatures noted are only indications of energy supplied, but these trends show the following.

1. The time to explosion for HMX and presumably other explosives is dependent on pressure. As pressure is increased the time to explosion decreases at a given temperature. This would tend to support Bowden's hot spot theory for gas bubbles in liquids. Decreasing the pressure would desensitize the explosive as the time to explosion would be greater hence there is more opportunity for energy dissipation.

2. The time-pressure relationship for HMX appears to follow equation (5). This is of the same form as that for the rate of burning-pressure relationship in propellant burning. The family of curves for HMX is of the same form as curves found in propellant burning.³² This correlation, that ignition time decreases and burning rate increases with pressure, seems to be a fairly obvious relationship.

If these two statements are true for most explosives of the CHNO group, as they are for HMX, we may propose the following hypothesis, that a controlling if not the controlling factor in burning is that conditions favorable for autoignition are present prior to the flame or burning front. This may be shown by the fact that the burning of a propellant or explosive may be quenched by a variation in the ambient pressure¹⁷ and that some propellents will not burn unless subjected to pressure.³² Also, it is known that the thermal conditions at the surface of a propellant can also determine if the substance will continue to burn.

If burning or ignition occurs in the vapor phase (as it appears to do in C-H-N-O type explosives) then the effect on burning and ignition can be explained by a variety of theories, most of which relate to

density of the gases at the burning front. This does not satisfactorily explain why HOLEX, a mixture containing a metal, also ignites early with increased pressure, unless the perchlorates or some other substances are the controlling factor in ignition.

If, however, we deal only with HMX, we may advance the following model. Energy delivered to the HMX causes it to begin to decompose. This energy is also enough to melt the explosive. Volatile substances from the decomposition react bimolecularly and the rate of this reaction is dependent on the ambient pressure and temperature. (These substances can be decomposition products or the HMX itself). Ignition occurs. The energy liberated by the flame in this burning influences, but is not the controlling factor in, the propagation of this burning, but burning will continue as long as the conditions for autoignition are present prior to the flame front. Our model correlates well with the theories of thermal ignition mentioned in this paper. Bowden specified a minimum size for gas bubbles below which ignition would not occur. If ignition occurs in the vapor phase in these gas bubbles, then our hypothesis, that a given pressure and temperature fixes an ignition time, will fix a volume for the gas bubble (if the energy is delivered by impact, or some other pulse). First, noting Chaiken's work¹⁶ in energy dissipation, there will be a certain maximum rate at which energy will be dissipated at the site of the gas bubble. Then, depending on the size of the bubble, there will be a pressure and temperature developed. If we are at a point where the pressure and temperature give an ignition time which is less than the time it takes to dissipate the energy which sustains this pressure and temperature, ignition occurs. Whether ignition is sustained, again depends on the pressure and temperature developed from the ignition itself.

From the results of this work, it appears that autoignition is one of the prime factors in both explosive initiation and in the rate of burning of propellents, and might form a bridge which connects the two phenomena.

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APPENDIX I

The auto-catalytic effects of H_2O and the oxide of nitrogen was shown as follows. Water is relatively insoluble in N.G. hence its amount may be controlled by the pressure of water vapor above the N.G.. It was shown that as decomposition progressed the solubility of water in N.G. increased. Three main stages of decomposition were noted.

- 1) Induction period, when pressure (water vapor above N.G.) remained almost constant.
- 2) A period of rapid fall in pressure
- 3) A period of accelerated pressure growth

In the induction period HNO_3 is produced from "waterless" decomposition and interaction of its products with H_2O and also as a result of hydrolysis, which is accelerated by the presence of acid.

In the second phase (when the HNO_3 concentration reaches several tenth's of a per cent) the water vapor passes directly into the N.G. and as a result of hydrolysis forms HNO_3 and the process becomes more autocatalytic.

In the third phase the HNO_3 concentration is high but the main effect is in oxidation-reduction reactions of the decomposition products and the N.G. with an abundant formation of gasses (brown, condensed, and non-condensing at room temperature). The speed of gas formation is approximately proportioned to the square of the pressure.

With high concentrations of H_2O the process is slowed, probably because of the subsequent diluting of the initial HNO_3 formed.

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14.

KEY WORDS

LINK A

LINK B

LINK C

ROLE

WT

ROLE

WT

ROLE

WT

AUTOIGNITION

THERMAL IGNITION

THERMAL DECOMPOSITION

HMX

GLASS TUBE SEALER

BURNING RATIO

IGNITION TIME

18

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